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PHOTOCONDUCTIVITY IN POLYACETYLENE

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ABSTRACT

An extensive study of the photoconductivity together with new measurements of the absorption coefficient of polyacetylene have been carried out. It is shown that the photoconductivity in trans-(CH)_x is controlled by localized states (inside the gap) induced either by isomerization or by dilute doping. The presence of such states and their effect on the photoconductivity of trans-(CH)_x is accounted for by the recently proposed soliton model.

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Despite great theoretical and technological interest in polyacetylene, $(CH)_x$, the basic features of its band structure have not been unambiguously resolved. Since photoconductivity and optical absorption data have frequently been used to infer information on the band structure of semiconductors, we have carried out such measurements on $(CH)_x$.

In this Letter we report the main results of an extensive study of the photoconductivity ($\Delta\sigma_{ph}$) and absorption coefficient (α) in $(CH)_x$. The absence of photoconductivity in cis- $(CH)_x$, despite the similarity in optical properties indicates that $\Delta\sigma_{ph}$ in trans- $(CH)_x$ is induced by isomerization. We find that isomerization generates states deep inside the gap that act as "safe traps" for minority carriers and thereby enhance the photoconductivity. Compensation of trans- $(CH)_x$ with ammonia appears to decrease the number of safe traps, whereas acceptor doping increases their number. Thus, chemical doping can be used to control the photoconductive response. The energy of the safe traps inside the gap is independent of the process used to generate them; indicative of an intrinsic localized defect level in trans- $(CH)_x$. A coherent picture based on the soliton model can explain these results, including the safe trapping.

The photoconductivity studies were carried out at room temperature on thin film samples (thickness of a few microns) polymerized directly on glass substrates. A surface cell configuration was employed using ohmic contacts made with

silverpaste or Electrodag conducting paints. The measurements were carried out in the range 0.6 - 3.0 eV using chopped light (13 Hz) from a tungsten lamp dispersed by a prism monochromator. Photocurrents were measured by phase sensitive detection of the voltage change across a resistor in series with the sample. Due to excellent thermal anchoring of the sample to the massive glass substrate, sample heating was found to be unimportant. ² Where necessary, corrections were made for transmitted light. The absorption coefficient studies were carried out on freshly grown semi-transparent thin films on glass substrates. All films were kept under vacuum or in an inert atmosphere.

In Fig. 1 the logarithm of the photocurrent (I_{ph}) in trans-(CH)_x is shown as a function of incident photon energy. The results were corrected for transmission (less than 15% over the whole spectrum for this sample). The inset in Fig. 1 shows a comparison of the same data (curve A) with results from three other samples of varying quality (see below) in order to point out the sample dependence of the photocurrent spectrum. Despite the large variation in the four sets of results, a distinct common feature is the rather sharp rise above 1.1 eV. The peak below 1.5 eV, which may be related to the 1.35 eV peak reported earlier, ³ is not seen in all samples.

Measurements of I_{ph} in cis-(CH)_x were attempted under similar conditions without success; no photocurrent has been detected in samples

of 80% cis-rich $(CH)_x$. In situ isomerization of the same film resulted in the sizeable I_{ph} shown in Fig. 1. The upper limit on I_{ph} in cis-(CH)_x is three orders of magnitude smaller than in trans-(CH)_x.

Since the dark conductivity can be varied by more than twelve orders
4
of magnitude through doping and compensation, we have investigated the corresponding effects on $\Delta\sigma_{ph}$. The data, after compensation with ammonia (NH_3) and after light doping with AsF_5 are also shown in Fig. 2. The curve labeled "compensated" is from the same sample as that labeled "initial result"; the "compensated data were obtained after exposure to ammonia sufficient to increase the dark resistance by several orders of magnitude. The curve labeled "acceptor doped" in Fig. 2 was obtained subsequently from the same sample after light doping with AsF_5 .

Compensation with ammonia appears to have two distinct effects. First, at energies near and below the edge, I_{ph} is decreased considerably relative to the photocurrent at higher energies. Second, the overall photoconductive response, including the energy region above the edge, decreases after compensation. Subsequent light doping with AsF_5 causes a uniform increase in the photoresponse. Note that the doping and compensation experiments cause I_{ph} to vary by more than two orders of magnitude with essentially no shift of the photoconductive edge. After compensation, the results for samples (C) and (D) (inset to Fig. 1) change to resemble that shown by curve (A). The effect of compensation is shown in more detail for sample (C) in the inset to Fig. 2.

The optical density of a carefully prepared uniform thin film is shown on Fig. 3 as a function of photon energy. The data were obtained with the film cooled to 77 K and have been normalized to show the absorption coefficient. Note that the absorption increases by more than two orders of magnitude at the sharp edge above 1.4 eV. The basic differences between this result and those reported earlier⁵ are the somewhat sharper edge and wider range in α due to the high quality $(\text{CH})_x$ film. The photocurrent results from Fig. 1 are also shown as $\log_{10} I_{ph}$ for comparison. We note that the photoconductivity edge is about 0.3 eV lower in energy than that of the absorption coefficient.

In addition to the main absorption, a weak absorption peak at about 0.9 eV is also evident in the data of Fig. 3. A second weak absorption at about 1.4 eV, reported previously,^() is detectable when the data are expanded to a proper scale. The oscillator strengths of these two weak absorptions are comparable and about three orders of magnitude smaller than that of the main absorption.

Summarizing: isomerization gives rise to photoconductivity in trans-($\text{CH})_x$ with an edge near 1.1 eV, about 0.4 eV below the absorption edge. Compensation and acceptor doping decrease and increase the photoconductivity, respectively, without changing the position of the edge.

The sharp rise in α together with the monotonic decrease above 2 eV^{5,6} has been attributed to the direct interband transition in a one-dimensional

(1d) band structure. The square root divergence of the joint density of states is presumably rounded by disorder and three-dimensional (3-d) interchain coupling.⁷ The results of Fig. 3 would then imply a 1-d direct band gap of about 1.6 eV with 3-d coupling and disorder decreasing the minimum gap to about 1.4 eV.

The peak in α near 2 eV is related to the transition from the peak in the density of states in the valence band (VB) to that of the conduction band (CB). The rounding appears to shift the position of the peaks in the VB and CB densities of states by about 0.2 eV. These results are sketched on a band diagram in the inset of Fig. 3, referring all energies to the edge of the valence band. The weak absorption near 0.9 eV would then correspond to a transition between the peak in VB density of states and a sharp level inside the gap; relative to the VB edge, the gap state occurs at about 0.7 eV. Similarly the second weak absorption peaking at 1.4 eV described above locates a second sharp level near 1.1 eV above the VB edge. Independent evidence of this second level is found in the structure observed in $\Delta\sigma_{ph}$ starting at about 1.1 eV with a maximum near 1.5 eV (see Figs. 1 and 2). The magnitude is sample dependent, and the peak is removed by compensation. We note that in this analysis we have ignored any shifts resulting from energy dependent matrix elements associated with the optical transitions.

Photoconductivity arises when photon absorption results in generation of electron-hole (e-h) pairs which can be separated in an electric field. Often, the photogenerated e-h pairs cannot be separated due to exciton formation or geminate recombination. In such a case one has absorption without photoconduction. Since the onset of $\Delta\sigma_{ph}$ is about 0.2 eV lower in energy than the onset of α , it is clear that the photoconduction process in trans-(CH)_x is intimately associated with the presence of states deep inside the gap. The fact that we have not been able to detect photoconductivity in cis-(CH)_x indicates that such states have been created in the isomerization process.

It is well-known that photoconductivity can be enhanced by the presence of states in the gap, so-called "safe-traps"; i. e. localized states that can capture electrons (minority carriers) and prevent recombination with mobile holes. As a result, the recombination time is lengthened considerably, thereby enhancing the photoconductivity. In the absence of trapping, and under steady state conditions

$$\Delta\sigma_{ph} = e\tau_R r (1 + b) \mu_e \quad (1)$$

where r is the carrier photogeneration rate, τ_R is the recombination lifetime, μ_e is the electron mobility and $b\mu_e$ is the hole mobility. In the case of safe trapped minority carriers (electrons), the additional photo-generated holes will increase with the number of trapped electrons. They will continue to produce a photocurrent until the trapped electrons eventually

recombine either directly or by primary excitation back into the conduction band. If the average time a minority carrier spends in a safe trap is τ_2 , and τ_1 ($\tau_1 < \tau_R$) is the average time before it is trapped, equation (2) then becomes:

$$\Delta\sigma_{ph}^* = e\tau_R \left[1 + b + b \frac{\tau_2}{\tau_1} \right] \mu_e \quad (2)$$

For $\tau_2 \gg \tau_1$, I_{ph} is enhanced by $\tau_2/\tau_1 \gg 1$ and the photoconductive decay is determined by τ_2 . In such a case $\Delta\sigma_{ph}^*$ would turn on at an energy corresponding to the transition from the VB to the safe trap state inside the gap, explaining the unusual result of Fig. 3. Preliminary measurements indicate a long decay time of order a few msec, consistent with these ideas. The sample dependent peak in the photocurrent spectrum (Figs. 1 and 2) corresponds to direct excitation of an electron from the VB peak into a safe trap. For such a direct excitation one obtains essentially 100% trapping, or $\tau_1 \rightarrow 0$.

Compensation of trans-(CH)_x would chemically fill the safe traps making them unavailable for photoexcited electrons. Acceptor doping would tend to generate new safe traps and/or empty the filled ones making them available for photoexcited electrons. The fact that (Fig. 2) acceptor doping can increase $\Delta\sigma_{ph}^*$ well beyond the undoped result while leaving the photoconductivity edge at the same energy is therefore critically important.

The observation that isomerization induces safe trap states inside the gap is suggestive of the applicability of the soliton model.^{10, 11, 12} In that picture the neutral soliton, S^0 , state at the center of the gap would be the safe trap. Since such a state would have an unpaired electron already in it, the energy required to excite an electron from the VB into S^0 (to create S^-) should be more than the energy of the initial state due to the Coulomb interaction. The result sketched in the inset of Fig. 3, suggests a correlation energy of about 0.3-0.4 eV. In the soliton picture the weak absorption turning on near 0.7 eV would be related to the excitation of an electron from the VB into the S^0 state at the center of the gap. Such a transition would require the presence of positively charged solitons, S^+ , as inferred from the thermopower results.¹¹

The identification of the safe traps as neutral solitons suggests a more detailed understanding of the long lifetime, τ_2 .¹³ Due to the difference in spatial extent¹² of charged and neutral solitons, the transition of a safe trapped electron to the VB or CB would require a major lattice deformation. As a result, such transition rates would be slowed by an orthogonality factor similar to that which arises in polaron theory. Moreover, even after excitation to the nearby CB, calculations¹¹ show that direct (band edge) radiative recombination is forbidden in the vicinity of a soliton. Thus, although considerable detailed theoretical work is required, it may be possible to understand the safe trapping in terms of a basic model of the coupled electron-lattice system.

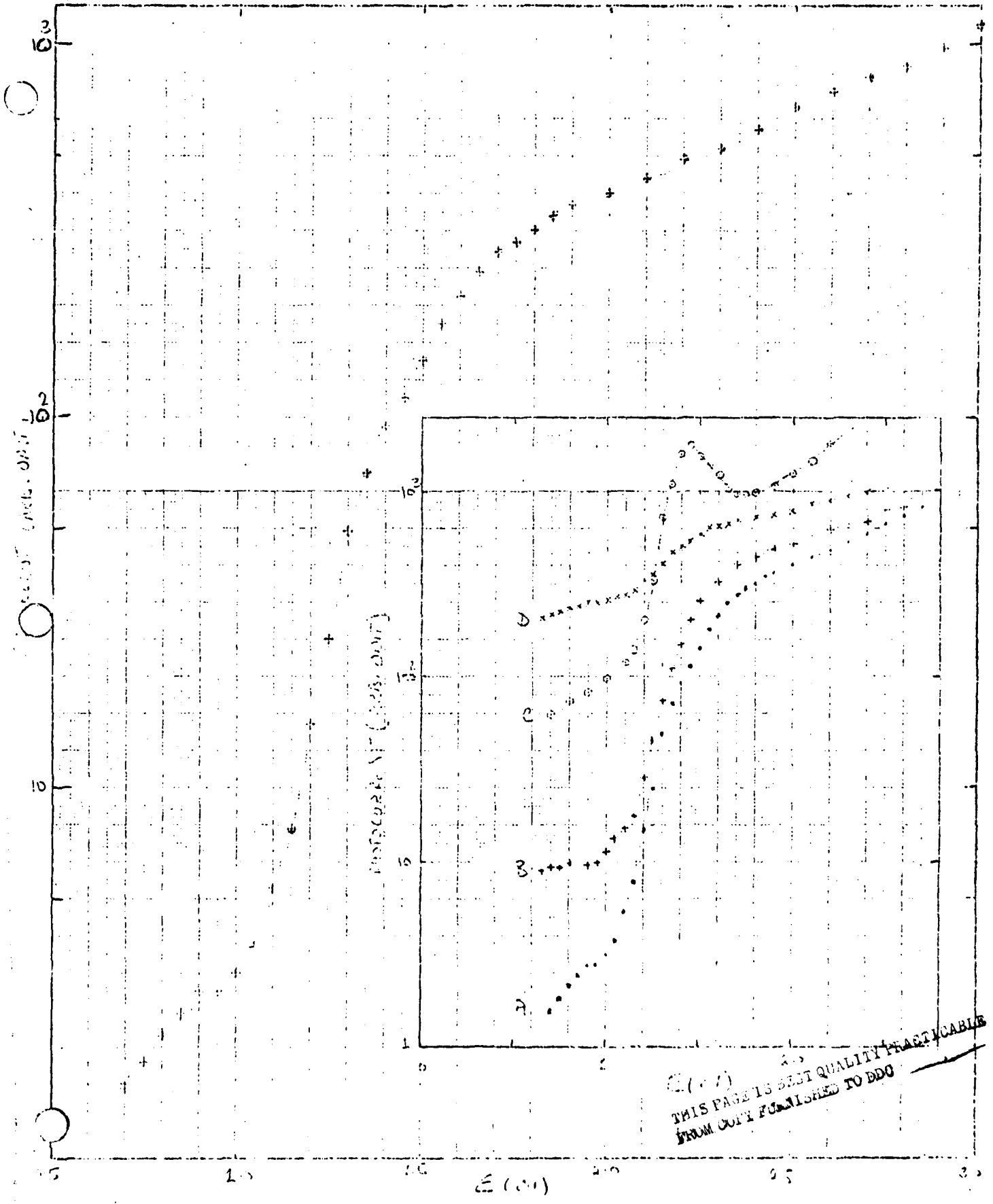
In conclusion, we have shown that the photoconductivity in trans-(CH)_x is controlled by localized states (inside the gap) induced either by isomerization or by dilute doping. The presence of such states and their effect on the photoconductivity of trans-(CH)_x is ~~only~~ accounted for by the soliton model.

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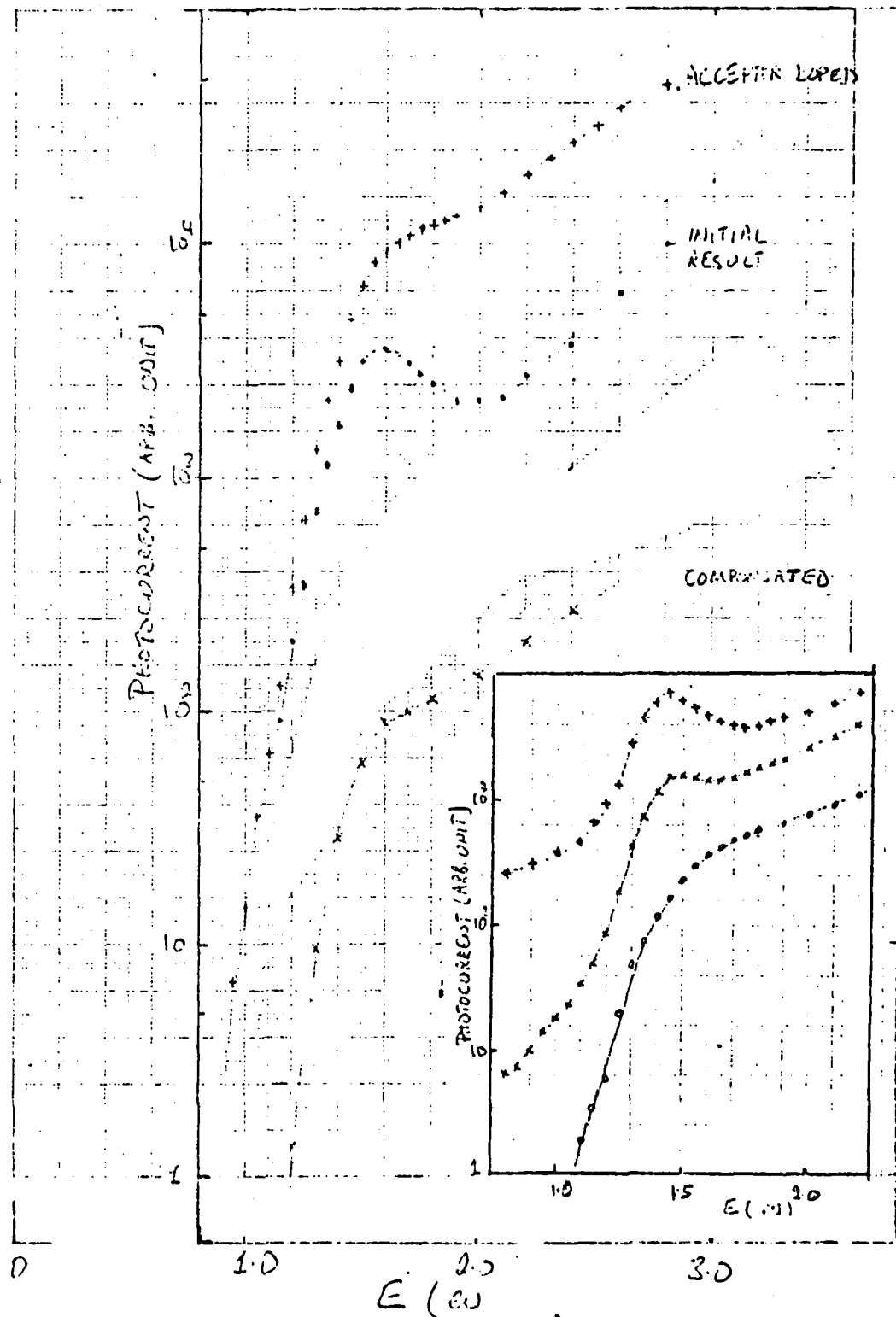


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